

RY

## Cyanide Chemistry

### Cyanide Species

The term cyanide refers to a singularly charged anion consisting of one carbon atom and one nitrogen atom joined with a triple bond,  $\text{CN}^-$ . The most toxic form of cyanide is free cyanide, which includes the cyanide anion itself and hydrogen cyanide,  $\text{HCN}$ , either in a gaseous or aqueous state. At a pH of 9.3 - 9.5,  $\text{CN}^-$  and  $\text{HCN}$  are in equilibrium, with equal amounts of each present. At a pH of 11, over 99% of the cyanide remains in solution as  $\text{CN}^-$ , while at pH 7, over 99% of the cyanide will exist as  $\text{HCN}$ . Although  $\text{HCN}$  is highly soluble in water, its solubility decreases with increased temperature and under highly saline conditions. Both  $\text{HCN}$  gas and liquid are colorless and have the odor of bitter almonds, although not all individuals can detect the odor.

Cyanide is very reactive, forming simple salts with alkali earth cations and ionic complexes of varying strengths with numerous metal cations; the stability of these salts is dependent on the cation and on pH. The salts of sodium, potassium and calcium cyanide are quite toxic, as they are highly soluble in water, and thus readily dissolve to form free cyanide. Operations typically receive cyanide as solid or dissolved  $\text{NaCN}$  or  $\text{Ca}(\text{CN})_2$ . Weak or moderately stable complexes such as those of cadmium, copper and zinc are classified as weak-acid dissociable (WAD). Although metal-cyanide complexes by themselves are much less toxic than free cyanide, their dissociation releases free cyanide as well as the metal cation which can also be toxic. Even in the neutral pH range of most surface water, WAD metal-cyanide complexes can dissociate sufficiently to be environmentally harmful if in high enough concentrations.

Cyanide forms complexes with gold, mercury, cobalt and iron that are very stable even under mildly acidic conditions. However, both ferro- and ferricyanides decompose to release free cyanide when exposed to direct ultraviolet light in aqueous solutions. This decomposition process is reversed in the dark. The stability of cyanide salts and complexes is pH dependent, and therefore, their potential environmental impacts and interactions (i.e. their acute or chronic effects, attenuation and re-release) can vary.

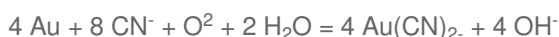
Metal cyanide complexes also form salt - type compounds with alkali or heavy metal cations, such as potassium ferrocyanide ( $\text{K}_4\text{Fe}(\text{CN})_6$ ) or copper ferrocyanide ( $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ ), the solubility of which varies with the metal cyanide and the cation. Nearly all alkali salts of iron cyanides are very soluble, upon dissolution these double salts dissociate and the liberated metal cyanide complex can produce free cyanide. Heavy metal salts of iron cyanides form insoluble precipitates at certain pH levels.

The cyanide ion also combines with sulfur to form thiocyanate,  $\text{SCN}^-$ . Thiocyanate dissociates under weak acidic conditions, but is typically not considered to be a WAD species because it has similar complexing properties to cyanide. Thiocyanate is approximately 7 times less toxic than hydrogen cyanide but is very irritating to the lungs, as thiocyanate chemically and biologically oxidizes into carbonate, sulfate and ammonia.

The oxidation of cyanide, either by natural processes or from the treatment of effluents containing cyanide, can produce cyanate,  $\text{OCN}^-$ . Cyanate is less toxic than  $\text{HCN}$ , and readily hydrolyzes to ammonia and carbon dioxide.

### Cyanidation

The process of extracting gold from ore with cyanide is called cyanidation. The reaction, known as Elsner's Equation, is:



Although the affinity of cyanide for gold is such that it is extracted preferentially, cyanide will also form complexes with other metals from the ore, including copper, iron and zinc. The formation of strongly bound complexes such as those with iron and copper will tie up cyanide that would otherwise be available to dissolve gold.

Copper cyanides are moderately stable; their formation can cause both operational and environmental concerns, as wastewater or tailings from such operations may have significantly higher cyanide concentrations than would otherwise be present in the absence of copper.

High copper concentrations in the ore increase costs and lower recovery efficiencies by requiring higher cyanide application rates to compensate for reagent that complexes with copper rather than gold.

Cyanidation is also adversely affected by the presence of free sulfur or sulfide minerals in the ore. Cyanide will preferentially leach sulfide minerals and will react with sulfur to produce thiocyanate. These reactions will also enhance the oxidation of reduced sulfur species, increasing the requirement for lime addition to control the pH at a sufficient level to avoid the volatilization of hydrogen cyanide (HCN).

Cyanide chemistry is complex, and those seeking additional information may find the list of reference materials found at the Code's website helpful: [References](#).